

**REMARKS**

In response to the final Office Action of January 2, 2008, Applicants have amended the claims, which when considered with the following remarks, is deemed to place the present application in condition for allowance. Favorable consideration and allowance of all pending claims is respectfully requested. The amendments to the claims have been made in the interest of expediting prosecution of this case. Applicants reserve the right to prosecute the same or similar subject matter in this or another application.

Claims 1-75 are pending in this application. By this Amendment, (1) Claims 1, 18 and 43 have been amended to incorporate the limitations of Claims 12, 24 and 52, respectively, (2) Claims 12, 24, 38 and 52 have been cancelled without prejudice, (3) Claims 13, 25 and 43 have been amended to correct the claim dependency and (4) Claims 63-75 are allowed. Accordingly, Claims 1-11, 13-23, 25-37, 39-51 and 53-75 are now under examination. Applicants respectfully submit that no new matter has been added to this application. Moreover, it is believed that the application presenting the claims herein is in condition for immediate allowance.

In the last Office Action mailed January 2, 2008, the Examiner rejected Claims 1-11, 14-23, 26-37, 39-40, 42-45, 49-51 and 54-62 under 35 U.S.C. §102(b) as being anticipated by Price U.S. Patent No. 3,140,997 ("Price"). Of these claims, Claims 1, 18 and 43 have been amended to incorporate the limitations of unrejected Claims 12, 24 and 52, respectively. Accordingly, this rejection is deemed moot. Therefore, withdrawal of the rejection of Claims 1-11, 14-23, 26-37, 39-40, 42-45, 49-51 and 54-62 as presented herein under 35 U.S.C. §102(b) is respectfully requested.

In the last Office Action mailed January 2, 2008, the Examiner rejected Claims 1-11, 14-23, 26-37, 39-40, 42-45, 48-51 and 54-62 under 35 U.S.C. §103(a) as being obvious over Price. Of these claims, Claims 1, 18 and 43 have been amended to incorporate the limitations of unrejected Claims 12, 24 and 52, respectively. Accordingly, this rejection is deemed moot. Therefore, withdrawal of the rejection of Claims 1-11, 14-23, 26-37, 39-40, 42-45, 48-51 and 54-62 as presented herein under 35 U.S.C. §103(a) is respectfully requested.

In the last Office Action mailed January 2, 2008, the Examiner rejected Claims 1-62 under 35 U.S.C. §103(a) as being unpatentable over Price in view of Valcho et al. U.S. Patent No. 4,601,837 ("Valcho et al.").

Nowhere does Price disclose or suggest a stable colloidal suspension comprising "(a) a dispersed phase comprising *a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ...* and, (b) an oil phase comprising one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and a diluent oil, *wherein the stable colloidal suspension is substantially clear*" as presently recited in independent amended Claim 1.

Rather, Price discloses a process for preparing a colloidal molybdenum complex which involves extracting a molybdenum compound from an acidic aqueous solution with a ketone, dispersing the resulting ketone extract containing a molybdenum compound in an oil-soluble basic metal-containing dispersant and removing the ketone and water from the dispersion. Price further discloses that the molybdenum compound is dissolved in a minimum amount of water necessary for a complete solution. Price goes on to state that sufficient mineral acid such as HCl is added to the solution to produce a solution having a normality of 2 to 12 and preferably 4 to 8.

It is submitted that one skilled in the art of chemistry would readily understand that the pH of a solution having a normality of 2 to 12 would be less than 2.

However, at a pH of less than 2, any polymolybdate present in the solution would necessarily breakdown into a non-polymeric molybdate. This is evidenced in, for example, Molybdenum: The Element and Aqueous Solution Chemistry, Volume 36.1, pp. 1256-1264 which states that "The incidence of protonation at pH ~ 7 triggers polymerization. Polymeric forms play a dominant role in the chemistry of Mo<sup>VI</sup> from pH 7 down to 2. At pH 2 to 1 (depending on the concentration) breakdown of polymers to give dimeric and monomeric octahedral forms occurs, where the latter are often referred to as [Mo(OH)<sub>6</sub>]." As the Examiner noted in the last Office Action that this reference was not seen, Applicants are re-submitting this reference as Exhibit 1 (as attached herein). Thus, any polymeric form of a molybdate that may be present would necessarily breakdown and no longer be in its polymeric form. Hence, the structures formed in Price in the initial reaction with high strength acid will not even result in hydrated polymolybdates. Furthermore, it is to be noted that, in Price, the dispersion of ketone extract and oil-soluble dispersant is heated to 200°F and then heating is continued to 350°F. Clearly, one could not expect such high temperature treatment of the molybdenum compounds to result in a species which could be described as "hydrated". Accordingly, the aqueous acidic solutions disclosed in Price would not contain (a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ... and, (b) an oil phase comprising one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and a diluent oil.

In fact, the aqueous acidic solutions disclosed in Price would simply be an aqueous acidic solution containing a *molybdenum compound* in which the *molybdenum compound* is then extracted from the acidic aqueous solution with a ketone, dispersed in an oil-soluble basic metal-containing dispersant and the ketone and water are then removed from the dispersion. One skilled in the art would readily understand that removing the ketone and water from the solution in Price would result in very little, if any, ketone and water left in the solution. Example 4 of Applicants' specification clearly shows that too much removal of water results in a hazy, not substantially clear, colloidal suspension. As such, one skilled in the art would not look to Price to modify the colloidal molybdenum complex disclosed therein and arrive at the stable colloidal suspension comprising "(a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ... and (b) an oil phase comprising one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and a diluent oil" as presently recited in independent amended Claim 1.

In addition, with respect to Claim 18, nowhere does Price disclose or suggest a process for preparing a stable colloidal suspension comprising:

"mixing, under agitation, (a) an aqueous solution comprising one or more hydrated polymeric compounds selected from the group consisting of polymolybdates, polytungstates, polyvanadates, polyniobates, polytantalates, polyuranates, and mixtures thereof; (b) one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear” as presently recited in amended Claim 18.

Nor, with respect to Claim 43, does Price disclose or suggest a process for preparing a stable colloidal suspension comprising:

“mixing, under agitation, an (a) aqueous solution comprising (i) one or more monomeric compounds selected from the group consisting of molybdenum, tungsten, and vanadium containing compounds and (ii) an effective amount of an acid capable of at least partially polymerizing the one or more monomeric compounds; (b) one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and (c) a diluent oil to form a micro emulsion; and,

heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear” as presently recited in amended Claim 43.

Rather, as stated above, Price discloses a colloidal molybdenum complex obtained by extracting a *molybdenum compound* from an acidic aqueous solution with a ketone, dispersing the resulting ketone extract containing a molybdenum compound in an oil-soluble basic metal-containing dispersant and heating and stripping the dispersion with gases to remove the ketone and water from the dispersion. Price further discloses that “[a]fter a period of agitation for proper contact with the ketone and then a period of settling for separation, the ketone extract layer is added to a suitable dispersant.” Price goes on to state that the ketone and water are thereafter removed. Thus, Price does not disclose, much less suggest, the process set forth in

Claim 18, comprising “mixing, under agitation, (a) an aqueous solution comprising one or more hydrated polymeric compounds selected from the group consisting of polymolybdates, polytungstates, polyvanadates, polyniobates, polytantalates, polyuranates, and mixtures thereof; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and, heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear.” Nor does Price disclose, much less suggest, the process set forth in Claim 43, comprising “mixing, under agitation, an (a) aqueous solution comprising (i) one or more monomeric compounds selected from the group consisting of molybdenum, tungsten, and vanadium containing compounds and (ii) an effective amount of an acid capable of at least partially polymerizing the one or more monomeric compounds; (b) one or more dispersing agents and (c) a diluent oil to form a micro emulsion; and, heating the micro emulsion to a temperature to remove sufficient water so as to produce a stable colloidal suspension ... wherein the stable colloidal suspension is substantially clear.”

Valcho et al. do not cure and are not cited as curing the deficiencies of Price. Instead, Valcho et al. are merely cited for the disclosure that a polybutene succinic anhydride can be added to the reaction zone as a process aid in the manufacture of an overbased molybdenum-alkaline earth metal sulfonate to increase the efficiency of molybdenum incorporation and improve product clarity. However, as with the disclosure in Price, Valcho et al. likewise provide no suggestion or motivation of a stable colloidal suspension comprising “(a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... *polymolybdates* ... and, (b) an oil phase comprising one or more dispersing agents and a diluent oil, *wherein the stable colloidal suspension is substantially clear*” as generally recited in

independent Claims 1, 18 and 43. Thus, even by combining Price with Valcho et al. one skilled in the art would not arrive at the presently claimed stable colloidal suspension.

In order to meet the burden of proving a *prima facie* obviousness rejection, the Examiner has alleged that:

“It would have been obvious to one of ordinary skill in the art at the time of the instantly claimed invention to use the instantly claimed combination of ingredients and amounts thereof and the methods of making the instantly claimed compositions because they are encompassed by the patentee. It would have been obvious to one of ordinary skill in the art at the time of the instantly claimed invention to use the acids of claim 48 because they are encompassed by “mineral acids” of column 2, lines 32-35 and would not have give the chlorine content not desired by the patentee at column 2, lines 37-42. It would have been obvious to one of ordinary skill in the art at the time of the instantly claimed invention to use the instantly claimed polyalkylene succinic anhydrides as the dispersants of Price because Valcho et al. shows such dispersants to improve the efficiency of molybdenum incorporation into similar dispersions and to improve product clarity at column 2, lines 31-37 and these improvements would have been expected in the compositions of Price.”

As stated above, Price would not even obtain the claimed stable colloidal suspension containing (a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ... and, (b) an oil phase comprising one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and a diluent oil, and wherein the stable colloidal suspension is substantially clear. Rather, Price adds sufficient mineral acid to the molybdenum-containing solution to produce a solution having a normality of 2 to 12 and preferably 4 to 8, i.e., a solution having a pH which would be less than 2. However, as discussed above, at a pH of less than 2, any polymolybdate present in the solution would necessarily breakdown (as evidenced in Molybdenum: The Element and Aqueous Solution Chemistry, Volume 36.1, pp. 1256-1264

(Exhibit 1)). Thus, even though Price may appear to contain similar components in making the colloidal molybdenum complex disclosed therein as alleged by the Examiner, Price would not arrive at the claimed colloidal dispersion. Accordingly, one skilled in the art would not look to combine Price with Valcho et al. as their combination would not arrive at the claimed invention. As such, it is submitted that the Examiner has not made out a case of *prima facie* obviousness in rejecting Claims 1-62 over Price with Valcho et al.

Despite the fact that no *prima facie* case of obviousness exists, Applicants submit that the experimental work presented in the Nelson Rule 132 Declaration (Exhibit 2) constitutes evidence that the combination of Price with Valcho et al. would not arrive at the claimed invention. Specifically, the data in the Nelson Rule 132 Declaration were directed to presenting examples that compared the process exemplified within the broad scope of Price and Valcho et al. and the resulting product therefrom with Applicants' claimed processes and colloidal suspension. As can readily be seen in Comparative Examples 1 and 2 set forth in the Declaration, a black solid product was obtained for each example. The results of these examples therefore clearly show how Price would not produce the claimed stable colloidal suspension containing (a) a dispersed phase comprising a major amount of one or more dispersed hydrated polymeric compounds selected from ... polymolybdates ... and, (b) an oil phase comprising one or more dispersing agents selected from the group consisting of polyalkylene succinic anhydrides, non-nitrogen containing derivatives of a polyalkylene succinic anhydride and mixtures thereof and a diluent oil, and wherein the stable colloidal suspension is substantially clear.

In view of the experimental data presented in the Nelson Rule 132 Declaration and the foregoing explanation of their significance, and given what has previously been said with respect to the Price and Valcho et al. disclosures, there is nothing in Price and Valcho et al., either alone



or in combination, which would lead one skilled in the art to look to the polyalkylene succinic anhydrides disclosed in Valcho et al. to modify the process disclosed in Price and arrive at the claimed invention. For the foregoing reasons, Claims 1-11, 13-23, 25-37, 39-51 and 53-62 are believed to be nonobvious, and therefore patentable, over Price in view of Valcho et al., no matter how these references are considered or combined.

For the foregoing reasons, Claims 1-11, 13-23, 25-37, 39-51 and 53-75 as presented herein are believed to be in condition for allowance. Such early and favorable action is earnestly solicited.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Michael E. Carmen", written in a cursive style.

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Enclosures

Exhibit 1: Molybdenum: The Element and Aqueous Solution Chemistry, Volume 36.1, pp. 1256-1264

Exhibit 2: Nelson Rule 132 Declaration

## 36.1

# Molybdenum: The Element and Aqueous Solution Chemistry

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## 36.1.1 THE ELEMENT

Molybdenum occurs chiefly as molybdenite,  $\text{MoS}_2$ , but also as molybdates  $\text{PbMoO}_4$  and  $\text{MgMoO}_4$ . The largest known deposits are in Colorado (USA), but it is also found in Canada and Chile. The natural abundance in the earth's crust ( $\sim 1.2$  p.p.m.) is about the same as that of tungsten, but is much less than of chromium (122 p.p.m.). The name in fact originates from the Greek *molybdos* meaning lead.

The Swedish chemist Scheele (1778) produced the oxide of a new element from (black)  $\text{MoS}_2$ , thereby distinguishing the element from graphite with which it had been confused. The metal was isolated by Hjelm in Sweden three to four years later by heating the oxide with charcoal. In the procedure now used to isolate the metal, the  $\text{MoS}_2$  component in ores is concentrated by flotation methods. The concentrate is then converted by roasting into  $\text{MoO}_3$ , which, after purification, is reduced with hydrogen. Reduction with carbon is avoided since carbides rather than the metal are obtained.

The chief use of molybdenum is in steels. The oxides and sulfides have some applications as catalysts. Molybdenum is the only element in the second and third transition series which appears to have a major role as a trace metal in enzymes. Several aspects of molybdenum chemistry have been widely studied in order to gain a better understanding of the biological relevance. Molybdenum is one of the few elements which currently has its own series of international conferences.<sup>1</sup>

Molybdenum and tungsten are similar chemically, although there are differences which it is difficult to explain. There is much less similarity in comparisons with chromium. In addition to the variety of oxidation states there is a wide range of stereochemistries, and the chemistry is amongst the most complex of the transition elements.

## 36.1.2 AQUEOUS SOLUTION CHEMISTRY

### 36.1.2.1 General Introduction

Molybdenum has an extensive aqueous solution chemistry for oxidation states II through VI. It is unique in having aqua or aqua/oxo ions for all five states in acidic solution ( $\text{pH} < 2$ ). These are well defined in all but the  $\text{Mo}^{\text{VI}}$  case, the study of which is complicated by the existence of rapid equilibria involving protonated/deprotonated monomer/dimer (and higher) forms. The VI state is without question the most stable and in contrast to  $\text{Cr}^{\text{VI}}$  is only the mildest of oxidants. Compounds which have contributed to the development of the aqueous solution chemistry, including the aqua ions themselves, are considered under Section 36.1.2. It is only since 1971 that the aqua forms of oxidation state II–V ions have been identified, and

preparative as well as structural features defined.<sup>2</sup> The chemistry of aqua ions generally has a somewhat elevated position, since they are often regarded as a point of reference or prototype for the behaviour of a particular oxidation state. Since they are difficult to crystallize, structural data of derivative complexes are relevant. The simple aqua ions of oxidation states II–V are indicated in Table 1. The quite different structures of adjacent oxidation states are to be noted, which gives rise to an interesting and varied redox chemistry. All but  $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$  are diamagnetic and metal–metal bonding is a significant contributing feature.

Table 1 Summary of Aqua Ions of Molybdenum at pH < 2

Description	Formula	Mo—Mo bonding	Colour
$\text{Mo}_2^{\text{II}}$	$[\text{Mo}_2(\text{H}_2\text{O})_8]^{4+}$	Quadruple	Red
$\text{Mo}^{\text{III}}$	$[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$	None	Pale yellow
$\text{Mo}_2^{\text{III}}$	$[\text{Mo}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$	Triple	Green
$\text{Mo}_3^{\text{IV}}$	$[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$	Single	Red
$\text{Mo}_2^{\text{V}}$	$[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$	Single	Yellow
$\text{Mo}_x^{\text{VI}}$	Different forms $x = 1 \text{ and } 2$	None	Colourless

The three most often used 'lead in' compounds for the chemistry described are sodium molybdate,  $\text{Na}_2[\text{MoO}_4] \cdot 2\text{H}_2\text{O}$ , molybdenum hexacarbonyl,  $[\text{Mo}(\text{CO})_6]$ , and potassium hexachloromolybdate,  $\text{K}_3[\text{MoCl}_6]$ . Synthesis of II and III state complexes generally requires rigorous  $\text{O}_2$ -free techniques, using a range of methods from those involving Schlenk apparatus to the use of  $\text{N}_2$  or Ar gas, syringes, Teflon tubing and/or stainless steel needles, and rubber seals. In some cases solutions of IV and V state complexes must also be stored  $\text{O}_2$  free. Perchlorate cannot be used with II and III aqua ions, and also appears to oxidize some trimeric  $\text{Mo}^{\text{IV}}$  ions on leaving overnight. Instead weakly coordinating, redox inactive and strongly acidic trifluoromethanesulfonic acid,  $\text{CF}_3\text{SO}_3\text{H}$  (abbreviated HTFMS or triflate), or *p*-toluenesulfonic acid,  $\text{C}_6\text{H}_4(\text{Me})\text{SO}_3\text{H}$  (abbreviated HPTS), finds wide usage. Methanesulfonic acid,  $\text{MeSO}_3\text{H}$ , has also been used.

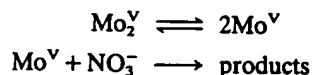
### 36.1.2.2 Oxidation State II

The aqueous chemistry of the II state is dominated by dimeric complexes. The latter constitute the largest group of compounds of any element containing quadrupole bonds, a subject extensively covered in the Cotton and Walton text.<sup>3</sup> Soon after the recognition of the quadruple bond in  $[\text{Re}_2\text{Cl}_8]^{2-}$  in 1964 the structure of  $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ , Figure 1, was published (Mo—Mo distance 2.09 Å).<sup>4</sup> The  $[\text{Mo}_2\text{Cl}_8]^{4-}$  complex, Figure 2, is obtained by treating  $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$  in aqueous KCl solution with 12 M HCl at 0°C when crystals of  $\text{K}_4[\text{Mo}_2\text{Cl}_8] \cdot 2\text{H}_2\text{O}$  are obtained. Similarly the bromo analogue  $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$  has been isolated. There are no bridging ligands and in both cases the Mo—Mo distance remains short (2.14 Å), consistent with retention of a quadruple metal–metal bond.<sup>5</sup> For comparison, typical M—M distances for quadruply bonded dimeric  $d^4$  complexes are 2.21 Å (for  $[\text{W}_2(\text{O}_2\text{CCF}_3)_4]$ ), 2.19 Å (for  $[\text{Tc}_2(\text{O}_2\text{CCMe}_3)_4\text{Cl}_2]$ )<sup>7</sup> and 2.2 Å (for  $\text{K}_2[\text{Re}_2\text{Cl}_8] \cdot 2\text{H}_2\text{O}$ ).<sup>3,4b</sup> The  $d^4$ – $d^4$  technetium complex is the only  $\text{Tc}^{\text{III}}$  example for which there is structural information, and the ease with which  $[\text{Tc}_2\text{Cl}_8]^{3-}$  rather than  $[\text{Tc}_2\text{Cl}_8]^{2-}$  is obtained is at present puzzling. The range of metal–metal distances in  $\text{Mo}_2^{\text{II}}$  complexes (2.04–2.18 Å) is much smaller than that observed in  $\text{Cr}_2^{\text{II}}$  (1.83–2.54 Å).<sup>3</sup>

Examples of monomeric  $\text{Mo}^{\text{II}}$  complexes are much less common. It has been demonstrated that the  $[\text{Mo}(\text{CN})_7]^{5-}$  ion has a pentagonal bipyramidal structure. Other examples are nitrosyl (i.e. isocyanide) complexes  $[\text{Mo}(\text{CNR})_7]^{2+}$ , which has a capped trigonal prismatic structure and the diarsine complex  $[\text{Mo}(\text{diars})_2\text{X}_2]$ .

The acetate complex  $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$  is obtained by heating  $[\text{Mo}(\text{CO})_6]$  with glacial acetic acid or a mixture of the acid and its anhydride.<sup>8</sup> Yields are low (15–20%), but can be improved (~80%) when diglyme is used as solvent.<sup>9</sup> The low yields are the result of the formation of trinuclear  $\text{Mo}^{\text{IV}}$  complexes of the type  $[\text{Mo}_3\text{X}_2(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]^{4+}$ , where the  $\text{Mo}_3\text{X}_2$  unit is a trigonal bipyramid with capping groups X either O or CMe (alkylidene).

[Mo<sub>2</sub>O<sub>4</sub><sup>2+</sup>] consistent with a mechanism shown in equations (30) and (31). From EPR measurements it has been confirmed that mononuclear Mo<sup>V</sup> is present.



Pulse radiolysis studies on [Mo<sub>2</sub>O<sub>4</sub>(edta)]<sup>2-</sup>, [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>(edta)]<sup>2-</sup>, [Mo<sub>2</sub>O<sub>4</sub>(cys)<sub>2</sub>]<sup>2-</sup> and [Mo<sub>2</sub>O<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> at pH ~6, in which the Mo<sub>2</sub><sup>V</sup> is reduced with e<sub>eq</sub><sup>-</sup> and Zn<sup>+</sup> to the Mo<sup>IV,V</sup> mixed-valence form have been reported.<sup>145</sup> The latter absorbs in the visible range (ε 300–500 M<sup>-1</sup> cm<sup>-1</sup> per dimer). In the absence of O<sub>2</sub> the decay is relatively slow (t<sub>1/2</sub> ~5–10 s), and does not result in Mo<sup>III</sup> production. With O<sub>2</sub> present there is rapid (~10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>) oxidation back to Mo<sub>2</sub><sup>V</sup>.

Inner-sphere paths are observed in the Cr<sup>2+</sup> reduction of 10<sup>-4</sup>–10<sup>-3</sup> M solutions of Mo<sub>2</sub><sup>V</sup>, [Mo<sub>2</sub>O<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, and of Mo<sub>3</sub><sup>V</sup>, [Mo<sub>3</sub>O<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup>, at 25 °C, I = 2.0 M (NaPTS).<sup>146</sup> In 1.9 M HPTS and with [Cr<sup>2+</sup>] in a greater than ten-fold excess of Mo<sub>2</sub><sup>V</sup>, the reaction proceeds via a grey-green Cr-containing intermediate (~1 min), to give a product with the Mo<sub>2</sub><sup>III</sup> spectrum (~24 h). The rate law for formation of the intermediate is of the form k<sub>1</sub>[Cr<sup>2+</sup>]<sup>2</sup>[Mo<sub>2</sub><sup>V</sup>][H<sup>+</sup>], with k<sub>1</sub> = 9.1 × 10<sup>3</sup> M<sup>-3</sup> s<sup>-1</sup>. Decay of the intermediate is independent of Cr<sup>2+</sup> and can be expressed as k<sub>2</sub>[intermediate][H<sup>+</sup>]. The rate constant k<sub>2</sub> = 2.0 × 10<sup>-5</sup> M<sup>-1</sup> s<sup>-1</sup> is believed to correspond to a process involving loss of Cr<sup>III</sup>. With a Cr<sup>2+</sup>:Mo<sub>2</sub><sup>V</sup> ratio of reactants of 2:1 evidence for two intermediates is obtained (~1 min), one (green in colour) giving a Cr:Mo ratio of 1:1, and the other the same as that generated in the reaction of excess Cr<sup>2+</sup> with Mo<sub>2</sub><sup>V</sup> giving a Cr:Mo ratio of 2:1. Some 30% of the Mo remains as Mo<sub>2</sub><sup>V</sup>. Over longer periods (~22 h) 60–70% overall conversion to Mo<sub>3</sub><sup>IV</sup> is observed, and 24–30% of the Mo is present as Mo<sub>2</sub><sup>V</sup>. In separate experiments, with Cr<sup>2+</sup> in a greater than ten-fold excess, Mo<sub>3</sub><sup>IV</sup> is reduced to Mo<sup>III,III,IV</sup> in a two-stage process, complete within 1 min, and then through to Mo<sub>3</sub><sup>III</sup> (~40 min). Reduction of Mo<sub>2</sub><sup>V</sup> to either Mo<sub>2</sub><sup>III</sup> or Mo<sub>3</sub><sup>III</sup> is observed therefore, depending on whether a single addition of excess Cr<sup>2+</sup> or successive additions of Cr<sup>2+</sup> are made.

### 36.1.2.6 Oxidation State VI

The solution chemistry of the Mo<sup>VI</sup> state has been an area of intense research activity for several decades. It is dominated by the isopolymolybdate and heteropolymolybdate forms,<sup>147</sup> brief mention of which is included here. Such studies remain an active area of research with applications in the area of industrial catalysis.<sup>1</sup> More than 65 elements from all groups of the Periodic Table (except the rare gases) are implicated as heteroatoms in such structures.<sup>147</sup> In addition to the text by Pope,<sup>147</sup> a review of isopolyanions has appeared.<sup>148</sup> An overview on the hydrolysis of cations is also relevant.<sup>149</sup> At pH > 7 Mo<sup>VI</sup> exists as the monomeric tetrahedral [MoO<sub>4</sub>]<sup>2-</sup> ions. Polymers are generated by conversion of tetrahedral Mo<sup>VI</sup> to octahedral forms in which there is edge, corner and (occasionally) face sharing of coordinated O<sup>2-</sup> ions between adjacent Mo atoms. In the absence of heteropolyanions protonation to give [HMoO<sub>4</sub>]<sup>-</sup>, more precisely [MoO<sub>3</sub>(OH)]<sup>-</sup> (pK<sub>a</sub> 3.47 in 1 M HCl), is followed by a second protonation to give [H<sub>2</sub>MoO<sub>4</sub>] (pK<sub>a</sub> 3.7 in 1 M NaCl). The latter at least (possibly both) is believed to be octahedral and is sometimes referred to as [Mo(OH)<sub>6</sub>] although other formulations have been suggested.<sup>150</sup> The incidence of protonation at pH ~ 7 triggers polymerization. Polymeric forms play a dominant role in the chemistry of Mo<sup>VI</sup> from pH 7 down to 2.<sup>151</sup> At pH 2 to 1 (depending on the concentration) break down of polymers to give dimeric and monomeric octahedral forms occurs, where the latter are often referred to as [Mo(OH)<sub>6</sub>]. The first protonation constant for [Mo(OH)<sub>6</sub>] has been determined.<sup>151b</sup> Singly and doubly charged cationic species are present in such solutions,<sup>151b,152</sup> and formulae which have been suggested include cis-[MoO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> and [Mo(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>. The cis-dioxo structure is found in a number of mononuclear coordination complexes, including cis-[MoO<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub>] (Et<sub>2</sub>dtc = N,N-diethylthiocarbamate),<sup>153</sup> cis-[MoO<sub>2</sub>(tox)<sub>2</sub>] (tox = thioxine or 8-mercaptoquinolate),<sup>154</sup> Λ-cis-[MoO<sub>2</sub>{(2R)-cysOMe}<sub>2</sub>] (cysOMe = 1-cysteine methyl ester)<sup>155</sup> and Λ-cis-[Mo<sub>2</sub>(S)-penOMe]<sub>2</sub> (penOMe = penicillamine methyl ester).<sup>156</sup> Two cis oxos are also present in the oxalato μ-oxo complex [(H<sub>2</sub>O)(C<sub>2</sub>O<sub>4</sub>)O<sub>2</sub>MoOMoO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]<sup>2-</sup> (Figure 31).<sup>157</sup> Facial trioxo coordination is on the other hand present in [MoO<sub>3</sub>dien] (dien = diethylenetriamine)<sup>158</sup> and the ethylenediaminetetraacetate complex [O<sub>3</sub>Mo(edta)MoO<sub>3</sub>]<sup>4-</sup><sup>159</sup> (Figure 32). Features of both structures are the MoO<sub>3</sub> bond angles (~106°) which are approaching those of a regular tetrahedron.

and the Mo—O(oxo) bond lengths of  $\sim 1.74 \text{ \AA}$  which indicate a bond order of two. The bond angles N—Mo—N ( $75^\circ$ ) for the dien complex, and N—Mo—O ( $73^\circ$ ) and O—Mo—O ( $75^\circ$ ) for the edta complex also suggest that the structures should be regarded as pseudotetrahedral. From Raman studies<sup>160</sup> it has been concluded that  $[\text{MoO}_3\text{dien}]$  is largely dissociated in water (equation 32), and reforms rapidly and quantitatively as a solid on addition of alcohol at pH  $\sim 7$ . Thus although it is necessary to replace an oxo ligand on  $[\text{MoO}_4]^{2-}$  the reaction occurs rapidly.

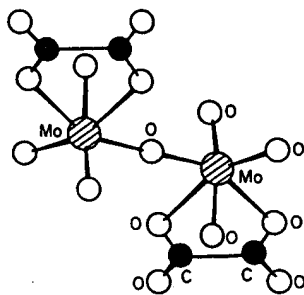
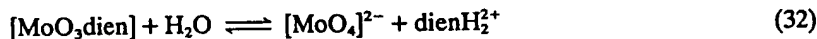


Figure 31 The structure of the  $\text{Mo}^{\text{VI}}$  complex  $[\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ <sup>157</sup>

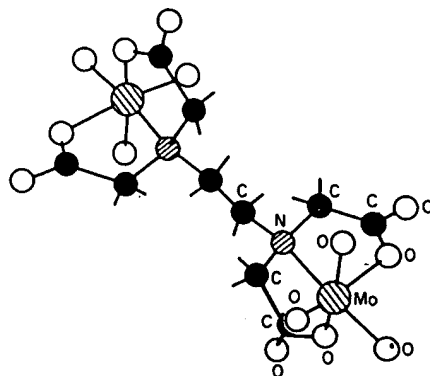
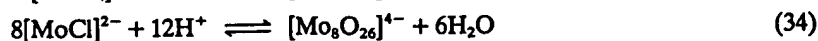
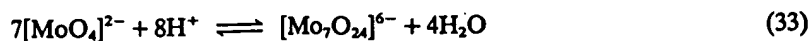


Figure 32 The structure of the  $\text{Mo}^{\text{VI}}$  complex  $[\text{O}_3\text{Mo}(\text{edta})\text{MoO}_3]^{4-}$ <sup>159</sup>

The polymeric forms obtained on decreasing the pH from 7 have been extensively investigated. For solutions with  $\text{Mo}^{\text{VI}}$  concentrations greater than  $10^{-3} \text{ M}$ , and pH in the range 3.0 to 5.5, the predominant form present is the heptamolybdate(VI) ion,  $[\text{Mo}_7\text{O}_{24}]^{6-}$ , sometimes referred to as paramolybdate (equation 33). Commercially available ammonium molybdate,  $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ , is obtained by crystallization of a solution of  $\text{MoO}_3$  in aqueous  $\text{NH}_3$ . In spite of numerous attempts, no intermediate has been unambiguously characterized in the aqueous conversion of  $[\text{MoO}_4]^{2-}$  to  $[\text{Mo}_7\text{O}_{24}]^{6-}$ . At pH  $< 4$  the  $\beta$ - $[\text{Mo}_8\text{O}_{26}]^{4-}$  octamolybdate form is obtained (equation 34). Representations of  $[\text{Mo}_7\text{O}_{24}]^{6-}$  and  $[\text{Mo}_8\text{O}_{26}]^{4-}$  are shown in Figure 33. The existence of significant amounts of the  $[\text{Mo}_8\text{O}_{26}]^{4-}$  ion has been controversial, but recent Raman and X-ray scattering<sup>161</sup> studies would seem to provide confirmation of its existence. Previously the interpretation of EMF data (pH 2–3) has been uncertain, because equally acceptable fits are given by a series of protonated  $[\text{Mo}_7\text{O}_{24}]^{6-}$  forms, as by a mixture of protonated  $[\text{Mo}_7\text{O}_{24}]^{6-}$  and  $[\text{Mo}_8\text{O}_{26}]^{4-}$ . From one set of stability constant determinations, Figure 34 has been obtained, indicating the distribution of different species. The ditetrahedral  $[\text{Mo}_2\text{O}_7]^{2-}$  ion has recently been identified in  $\text{Mg}[\text{Mo}_2\text{O}_7]$  and in the double salt  $\text{K}_2[\text{Mo}_2\text{O}_7] \cdot \text{KCl}$ .<sup>162,163</sup> These structures are to be contrasted with the crystalline product  $(\text{NH}_4)_2[\text{Mo}_2\text{O}_7]$ , obtained from hot aqueous ammonium molybdate solution after some hours, which consists of infinite chains of tetrahedral  $\text{MoO}_4$  and octahedral  $\text{MoO}_6$  units.<sup>164</sup>



## Molybdenum

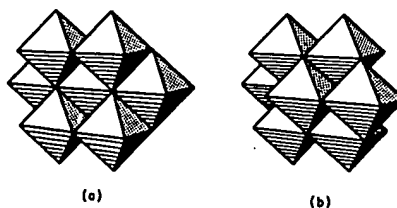


Figure 33 The structures of (a) heptamolybdate,  $[\text{Mo}_7\text{O}_{24}]^{6-}$ , and (b) octamolybdate,  $[\text{Mo}_8\text{O}_{26}]^{4-}$  (one  $\text{MoO}_4$  octahedron hidden)

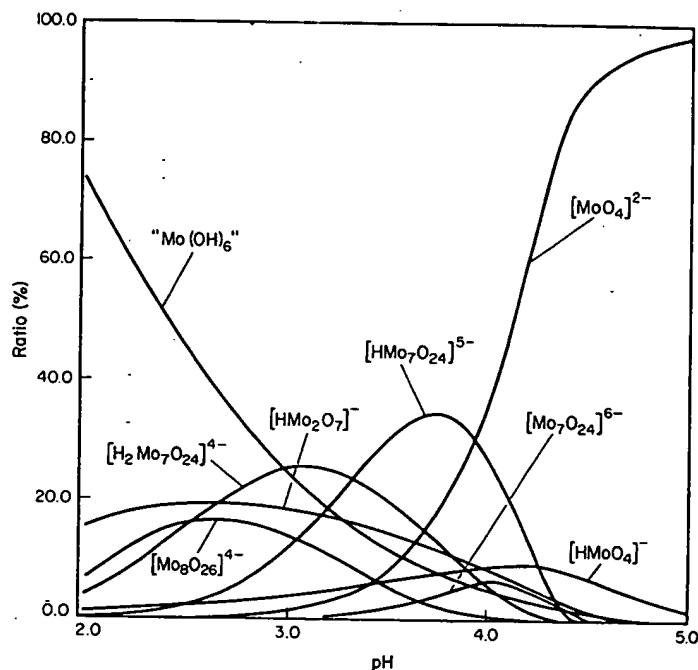
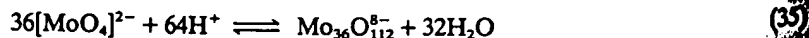


Figure 34 Distribution of  $\text{Mo}^{\text{VI}}$  forms with pH for a solution of  $5 \times 10^{-4}$  M molybdate at  $25^\circ\text{C}$ ,  $I = 1.0$  M (NaCl), as calculated by A. Nagasawa and R. Iwata (unpublished work) from data in ref. 151

Solutions of  $\text{Mo}^{\text{VI}}$  acidified to  $\text{H}^+ / [\text{MoO}_4]^{2-} \sim 1.8$  contain one or more very large polymolybdate structures. Earlier measurements based on ultracentrifugation and EMF studies,<sup>165</sup> through to a recent structure report,<sup>166</sup> are consistent with a formula  $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{18}]^{8-}$ . The reaction can be summarized as in equation (35). There are two seven-coordinate  $\text{Mo}^{\text{VI}}$  atoms in this structure. In all isopoly and heteropoly structures the metal ion does not lie at the centre of its polyhedron, but is displaced towards the exterior of the structure and towards a vortex or edge of its own polyhedron. Structures appear to be governed by electrostatic and radius-ratio principles as observed for extended ionic lattices. The  $\text{Mo}^{\text{VI}}$  tetrahedral radius is  $0.55 \text{ \AA}$  ( $0.56 \text{ \AA}$  for W), the octahedral radius  $0.73 \text{ \AA}$  ( $0.74 \text{ \AA}$  for W), and the radius of  $\text{O}^{2-}$  is  $1.40 \text{ \AA}$ .<sup>167</sup>



Important differences are observed in comparing the behaviour of  $\text{Mo}^{\text{VI}}$  and  $\text{W}^{\text{VI}}$ . Equilibria involving  $[\text{MoO}_4]^{2-}$  and polymolybdates in aqueous solution are established rapidly and are complete in a matter of minutes, whereas those for  $\text{W}^{\text{VI}}$  can take several weeks. The polyanions of tungsten are made up of  $\text{WO}_6$  octahedra, but in other respects the behaviour of  $\text{W}^{\text{VI}}$  solutions is quite different, and structurally the polyanions in one series do not have precise counterparts in the other. Known structures of isopolytungstates from aqueous solution include  $[\text{W}_4\text{O}_{16}]^{8-}$ ,  $[\text{W}_4\text{O}_{19}]^{2-}$ ,  $[\text{W}_{10}\text{O}_{32}]^{4-}$ ,  $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$  and  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ .<sup>147</sup> A number of other isopolymolybdate anions including  $[\text{Mo}_6\text{O}_{19}]^{2-}$ ,  $\alpha\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ , and  $[\text{Mo}_5\text{O}_{17}\text{H}]^{3-}$  can be stabilized in non-aqueous or mixed solvents.<sup>168</sup> The  $[\text{Mo}_2\text{O}_7]^{2-}$  ion is also obtained from acetonitrile solution. Tetrahedral coordination is retained in the latter.<sup>169</sup> There

two distorted tetrahedra in  $\alpha$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> above and below a crown of six octahedra formed edge sharing. A tetrahedron spanning a ring of four edge- and face-shared octahedra is also believed to be present in [Mo<sub>5</sub>O<sub>17</sub>H]<sup>3-</sup>.<sup>170</sup> The  $\alpha$  and  $\beta$  structures can coexist in solution, and a temperature dependent isomerization of  $\alpha$  into  $\beta$  has been observed.<sup>171</sup> Isopolymolybdates are generally colourless, and heteropoly forms can be coloured if another transition metal ion is present. Some other heteropolyanions can be coloured, for example that obtained by addition of ammonium molybdate to phosphoric acid to give ammonium hexamolybdo-phosphate, [NH<sub>4</sub>]<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>], which is yellow. The [Mo<sub>6</sub>O<sub>19</sub>]<sup>2-</sup> anion is unique for an isopolyanion in being yellow ( $\lambda_{\max}$  325 nm) and having a structure with a monocoordinated terminal oxo group rather than MoO<sub>2</sub> units. This ion is electrochemically reduced to the mixed valence [Mo<sub>6</sub>O<sub>19</sub>]<sup>3-</sup> and [Mo<sub>6</sub>O<sub>19</sub>]<sup>4-</sup> forms in DMF. Incorporation of the Mo<sup>V</sup> state in blue-red and yellow mixed-valence species formulated as [Mo<sub>2</sub>Mo<sup>V</sup><sub>4</sub>O<sub>18</sub>]<sup>2-</sup>, [Mo<sub>3</sub>Mo<sup>V</sup><sub>3</sub>O<sub>18</sub>]<sup>2-</sup> and [Mo<sub>2</sub>Mo<sup>V</sup><sub>4</sub>O<sub>17</sub>H]<sup>2-</sup> respectively has also been reported. The reduction of addenda atoms in heteropolyanions results in the formation of heteropoly blues, and gives rise to a vast chemistry. The added electrons are delocalized according to varying timescales over certain atoms and/or regions of the structure.

Because the surfaces of polyanions have some similarities to those of metal oxides, it is thought they may have some relevance in the area of heterogeneous catalysis. As a result a whole new area concerned with the synthesis and study of organic and organometallic derivatives of polyanions is being investigated.<sup>173</sup>

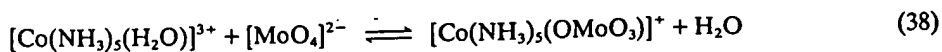
A kinetic investigation of the <sup>18</sup>O exchange between water and molybdate [MoO<sub>4</sub>]<sup>2-</sup> at pH > 11, [OH<sup>-</sup>] = 3 × 10<sup>-3</sup>–0.15 M, *I* = 1.00 M (NaClO<sub>4</sub>), has been carried out.<sup>174</sup> The rate law (equation 36) indicates paths involving reaction with H<sub>2</sub>O and OH<sup>-</sup> ( $k_1 = 0.33 \text{ s}^{-1}$ ,  $k_{\text{OH}} = 0.22 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C). The corresponding  $k_1$  values for [CrO<sub>4</sub>]<sup>2-</sup> (3.2 × 10<sup>-7</sup> s<sup>-1</sup>) and [WO<sub>4</sub>]<sup>2-</sup> (0.44 s<sup>-1</sup>) provide one of the few kinetic comparisons for Cr, Mo and W. The difference in rate constants is attributable to the larger enthalpy of activation in the case of chromate, reflecting stronger Cr<sup>VI</sup>—O bonds. It has to be borne in mind that there are other contributing paths for chromate, the full rate law having been determined as equation (37). The molybdate exchange cannot readily be studied by <sup>18</sup>O labelling at pH 11, because protonation is effective and much faster rates are observed.<sup>174</sup>

$$\text{Rate} = k_1[\text{MoO}_4^{2-}] + k_{\text{OH}}[\text{MoO}_4^{2-}][\text{OH}^-] \quad (36)$$

$$\text{Rate} = k_1[\text{CrO}_4^{2-}] + k_2[\text{HCrO}_4^-] + k_3[\text{H}^+][\text{HCrO}_4^-] + k_4[\text{HCrO}_4^-] + k_5[\text{HCrO}_4^-]^2 \quad (37)$$

Fast monomer–dimer equilibria involving Mo<sup>VI</sup> in 0.2–0.3 M HClO<sub>4</sub>, *I* = 3.0 M (LiClO<sub>4</sub>), have been studied by the temperature-jump method.<sup>176</sup> A major pathway involves rapid dimerization of a monomer form, referred to as [HMoO<sub>3</sub>]<sup>+</sup>, which might alternatively be written [MoO<sub>2</sub>(OH)(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> or a related form. At 25 °C, *I* = 3.0 M [LiClO<sub>4</sub>], rate constants are  $k_f = 1.71 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_b = 3.2 \times 10^3 \text{ s}^{-1}$ . Information has been obtained by the stopped-flow method for the interconversion of tetrahedral chromate and dichromate ions.<sup>177</sup> At pH 2–4 hydrogen chromate, [HCrO<sub>4</sub>]<sup>-</sup>, is specified as the reactant. From this and other similar studies on the substitution reactions of [HCrO<sub>4</sub>]<sup>-</sup> there is evidence for a dissociative process.<sup>178</sup> Further information concerning precise formulae of Mo<sup>VI</sup> in acidic solutions is required to enable more extensive comparisons.

Temperature-jump studies of Mo<sup>VI</sup> solutions at pH 5.50–6.75 have been reported for the monomer–heptamer and heptamer–octamer interconversions which are complete within a few milliseconds.<sup>179</sup> Molybdate as [HMoO<sub>4</sub>]<sup>-</sup> (here assumed to be tetrahedral) reacts with bidentate 8-hydroxyquinoline<sup>180</sup> and catechol,<sup>181</sup> to give octahedral products in net 4 → 6 conversions.<sup>180</sup> Table 4 summarizes the kinetic data, where different degrees of protonation of the ligating groups are indicated. For the reaction with edta a path assigned to the reaction of [H<sub>2</sub>edta]<sup>2-</sup> with [HMoO<sub>4</sub>]<sup>-</sup> gives a rate constant of 2.3 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>182</sup> A reaction in which the tetrahedral geometry of [MoO<sub>4</sub>]<sup>2-</sup> is retained is the rapid stopped-flow equilibration of molybdate with [Co(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>3+</sup> (pK<sub>a</sub> 6.3) at pH 7–8 (equation 38).<sup>183</sup>



Substitution is at the Mo<sup>VI</sup> centre with retention of the Co—O bond. The first-order [H<sup>+</sup>]-dependent term is consistent with [HMoO<sub>4</sub>]<sup>-</sup> as a reactant, and the [H<sup>+</sup>]-independent term is assigned to the reaction of [HMoO<sub>4</sub>]<sup>-</sup> with [Co(NH<sub>3</sub>)<sub>5</sub>OH]<sup>2+</sup>. An interesting situation arises in the reaction of [MoO<sub>4</sub>]<sup>2-</sup> with [Cr(edta)(H<sub>2</sub>O)]<sup>-</sup> at pH 7.3–8.7.<sup>184</sup> As in the case of

Table 4 Second-order Rate Constants for Reactions of  $[\text{HMoO}_4]^-$  at 25 °C

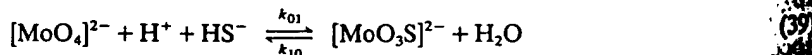
Ligand	Ionic strength	Coordination change at $\text{Mo}^{\text{VI}}$	$k \text{ (M}^{-1} \text{s}^{-1}\text{)}$
H-oxine	0.20	4→6	$4.5 \times 10^6$
H-oxine- $\text{SO}_3^-$	0.20	4→6	$3.9 \times 10^6$
oxine $^-$	0.20	4→6	$1.5 \times 10^8$
oxine- $\text{SO}_3^{2-}$	0.20	4→6	$4.0 \times 10^7$
H-catechol $^-$	0.10	4→6	$1.9 \times 10^8$
$\text{H}_2$ -edta	0.10	4→6	$2.3 \times 10^5$
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	1.0	4→4	$3.2 \times 10^5$
$[\text{Co}(\text{NH}_3)_5\text{OH}]^{2+}$	1.0	4→4	$6.6 \times 10^4$
$[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$	1.0	4→4	$3.1 \times 10^4$
$\text{HS}^-$	0.50	4→4	$1.3 \times 10^6$

H-oxine = 8-hydroxyquinoline.

H-oxine- $\text{SO}_3^-$  = 8-hydroxyquinoline-5-sulfonic acid.H-catechol $^-$  = product of first acid dissociation of catechol.

$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ , there are two terms for complex formation in the rate law, one of which can be assigned to the reaction of  $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$  with  $[\text{MoO}_4]^{2-}$  (rate constant  $21 \text{ M}^{-1} \text{s}^{-1}$ ). The second, which is first order in  $[\text{H}^+]$ , corresponds to replacement of the  $\text{H}_2\text{O}$  of  $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$  by  $[\text{HMoO}_4]^-$  ( $3.1 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$ ). Whereas the first is believed to correspond to replacement of the  $\text{H}_2\text{O}$  (labilized by the presence of the carboxylate) at the  $\text{Cr}^{\text{III}}$ , the latter, as in other cases corresponds to substitution at the  $\text{Mo}^{\text{VI}}$  centre. There are proton ambiguities however because the first reaction could also be assigned to the reaction of  $[\text{Cr}(\text{edta})\text{OH}]^{2-}$  ( $\text{p}K_a 7.4$ ) with  $[\text{HMoO}_4]^-$ . In all these examples the interpretation requires that there are pathways in which there is protonation of  $[\text{MoO}_4]^{2-}$  prior to complexation. Protonation labilizes at least one oxo ligand and may itself induce a 4→6 change in coordination to give a more labile species. Consistent with this, rates are much more rapid than for  $\text{H}_2^{18}\text{O}$  exchange with  $[\text{MoO}_4]^{2-}$ .

Tetrahedral sulfido or thiolate complexes are known for a number of  $d^0$  transition metal ions including  $\text{Mo}^{\text{VI}}$ .<sup>185</sup> Preparative procedures involve the reaction of solutions of oxyanions with  $\text{H}_2\text{S}$ . In addition to  $[\text{MoS}_4]^{2-}$  the mixed oxo/sulfido complexes  $[\text{MoOS}_3]^{2-}$ ,  $[\text{MoO}_2\text{S}_2]^{2-}$  and  $[\text{MoO}_3\text{S}]^{2-}$  are well characterized. Although the latter is difficult to obtain in a pure crystalline state, X-ray crystal structure information on  $(\text{NH}_4)_2[\text{MoS}_4]$  ( $\text{Mo}-\text{S} = 2.17 \text{ \AA}$ ),<sup>186</sup> and  $\text{Cs}_2[\text{MoOS}_3]$  ( $\text{Mo}-\text{S} = 2.18 \text{ \AA}$ ;  $\text{Mo}-\text{O} = 1.79 \text{ \AA}$ )<sup>187</sup> have been reported, and the  $\text{Mo}-\text{O}$  distance is slightly longer than in  $\text{Mo}^{\text{VI}}$  complexes  $\text{K}_2[\text{MoO}_4]$  ( $1.76 \text{ \AA}$ ),  $[\text{MoO}_3(\text{dien})]$  ( $1.74 \text{ \AA}$ ) and  $[\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$  ( $\text{Mo}-\text{O}_t 1.69 \text{ \AA}$ ). Bridged  $\text{Mo}^{\text{VI}} \mu$ -sulfido complexes do not appear to be formed and there are no counterparts in the polymeric (and heteropoly) species found from  $[\text{MoO}_4]^{2-}$ . Kinetic studies on the interconversion of  $[\text{MoO}_x\text{S}_{4-x}]^{2-}$  forms have been carried out.<sup>188</sup> The 1:1 equilibration of  $\text{H}_2\text{S}$  with  $[\text{MoO}_4]^{2-}$  can be expressed as in equation (39).



There are few quantitative studies with  $\text{H}_2\text{S}$  as a reactant, and some difficulties were experienced in choosing conditions appropriate to the study. At pH 9.2–10.2 (0.25 M  $\text{NH}_3/\text{NH}_4^+$  buffer),  $I = 0.50 \text{ M}$  (NaCl), plots of equilibration rate constants against  $[\text{MoO}_4^{2-}]$  are in accord with equation (40).

$$k_{\text{eq}} = k_f[\text{MoO}_4^{2-}] + k_b \quad (40)$$

The formation constant  $k_f$  is dependent on  $[\text{H}^+]$  giving  $k = 4.0 \times 10^9 \text{ M}^{-2} \text{s}^{-1}$ , and  $k_b$  for the reverse reaction is  $6.5 \times 10^{-3} \text{ s}^{-1}$ . Interpretation of  $k$  in terms of a reaction between  $[\text{HMoO}_4]^-$  and  $\text{HS}^-$  is preferred rather than the alternative of  $[\text{MoO}_4]^{2-}$  with  $\text{H}_2\text{S}$ , and on this basis a second-order rate constant of  $1.3 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$  is obtained, of similar magnitude to those listed in Table 4. Other formation rate constants for the different  $[\text{MoO}_x\text{S}_{4-x}]^{2-}$  ions have to be determined in the form of the experimental third-order rate constants since the relevant protonation constants are not known. For the rate law  $k[\text{MoO}_x\text{S}_{4-x}^{2-}][\text{HS}^-][\text{H}^+]$ ,  $k$  values range from  $4.0 \times 10^9 \text{ M}^{-2} \text{s}^{-1}$  for the reaction of  $[\text{MoO}_4]^{2-}$  to less than  $1.6 \times 10^6 \text{ M}^{-2} \text{s}^{-1}$  for  $[\text{MoOS}_3]^{2-}$ . Rate constants for aquation of  $[\text{MoO}_3\text{S}]^{2-}$  ( $6.5 \times 10^{-3} \text{ s}^{-1}$ ),  $[\text{MoOS}_3]^{2-}$  ( $\sim 5 \times 10^{-5} \text{ s}^{-1}$ ) and



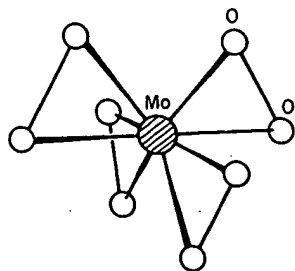


Figure 35 The structure of the  $\text{Mo}^{\text{VI}}$  peroxo complex,  $[\text{Mo}(\text{O}_2)_4]^{2-}$ <sup>190</sup>

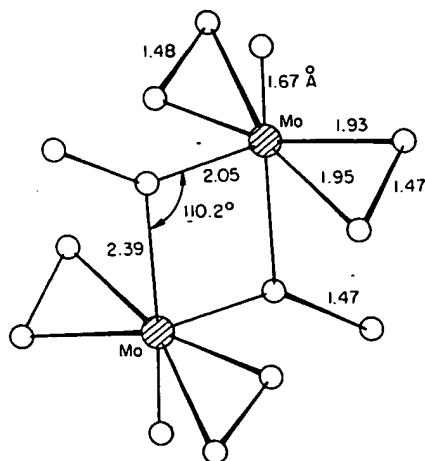


Figure 36 The structure of the  $\text{Mo}^{\text{VI}}$  peroxo/hydroperoxo complex  $[(\text{O}_2)_2\text{OMo}(\text{OOH})_2\text{MoO}(\text{O}_2)_2]^{2-}$ <sup>196</sup>

$10\text{S}_4]^{2-}$  ( $1.6 \times 10^{-6} \text{ s}^{-1}$ ) indicate a trend to smaller values as more sulfide ligands are introduced. The presence of sulfide does not appear to give a labilizing effect. Different crystalline phases can be separated from aqueous solutions of potassium molybdate(VI) following reaction with varying amounts of hydrogen peroxide, pH 4–8.<sup>189</sup> Crystal structure determinations of  $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$ ,<sup>190</sup>  $\text{K}_2[\text{O}\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}_2] \cdot \text{H}_2\text{O}$ ,<sup>190</sup>  $\text{K}_4[\text{Mo}_4\text{O}_{12}(\text{O}_2)_2]$ <sup>192</sup> and  $\text{K}_6[\text{Mo}_7\text{O}_{22}(\text{O}_2)_2] \cdot 8\text{H}_2\text{O}$ <sup>193</sup> have for example been reported. In all cases the  $\text{O}_2^{2-}$  is bound sideways to the metal, with O—O distances varying from 1.38 to 1.55 Å, but generally around 1.48 Å, which is the expected value for peroxide. The peroxo ligands in the dark red  $[\text{Mo}(\text{O}_2)_4]^{2-}$  compound (O—O distance 1.55 Å) are positioned tetrahedrally about the  $\text{Mo}^{\text{VI}}$  (Figure 35). A  $\text{Cr}^{\text{V}}$  analogue  $[\text{Cr}(\text{O}_2)_4]^{3-}$ , having a similar configuration (O—O distance 1.48 Å), is known. An interesting variation is the occurrence of hydroperoxide as a bridging ligand in  $(\text{pyH})_2[(\text{O}_2)_2\text{OMo}(\text{OOH})_2\text{MoO}(\text{O}_2)_2]$ ,<sup>194</sup> where the bridge has a pendant —O(OH)— arrangement (Figure 36). Only one other example of this structure is known in the  $\text{Co}^{\text{III}}$  complex  $[(\text{en})_2\text{Co}(\text{NH}_2, \text{O}_2\text{H})\text{Co}(\text{en})_2]^{4+}$ .<sup>195</sup> The complex  $\text{K}_2[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]$  is monomeric,<sup>196</sup> and to be regarded as five- or seven-coordinate depending whether the  $\text{O}_2^{2-}$  is assigned one or two coordination positions.

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